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THE SYNTHESIS AND PHOTODIMERIZATION OF 2H-2-BENZAZEPINE-1,3-DIONES

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Abstract—The photochemical dimerization of 2H-2-benzazepine-1,3-diones has been described. The structures of the major products are assigned as the head-to-tail, **5**, and the head-to-head, **7**, photodimers on the basis of the analysis of the coupling constants in the NMR spectra. In addition, the structures of the minor products and attempts to convert **5** to **7** are discussed.

While intense interest has developed in the chemistry of the 2-benzazepine and 1,4-benzodiazepine ring systems during the past decade,[1] only recently have the photochemical reactivities of these heterocycles been explored.[2] In contrast to a variety of di- and tetrahydro analogs, members of the unsaturated 2H-2-benzazepine-1,3-dione ring system, **3**, were unknown at the start of this investigation.[3] Interest in **3** stems from its potential utility in the synthesis of other novel heterocycles and as a semiflexible substrate in the study of photodimerization and cycloaddition processes. We now wish to report a convenient synthesis of that ring system and to describe the formation and structures of products formed during its photolysis.

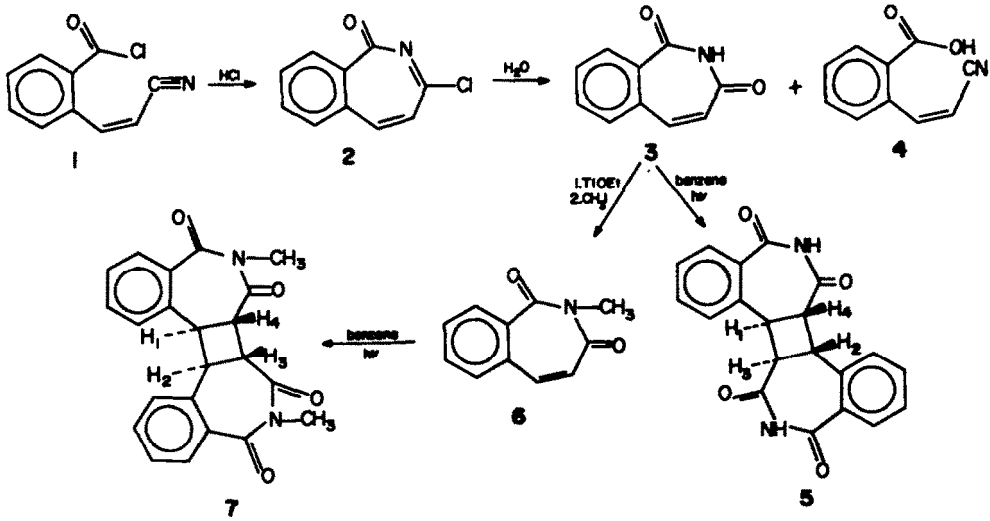
RESULTS AND DISCUSSION

Since the most direct approach to **3**, from 2-isonitroso-1-naphthol affords only the products of ring cleavage,[3] an alternate synthesis, via the recently reported 3-chloro-1H-2-benzazepin-1-one **2**[4] was investigated (Scheme 1). Thus, acid catalyzed cyclization of 2-(chloroformyl)-*cis*-cinnamonitrile **1** afforded the "chloroimide" **2**,[5] which was hydrolyzed without purification to a mixture of the desired 2H-2-benzazepine-1,3-dione, **3**,[6] and the isomeric cleaved acid, **4**. Subsequent difficulties in the methylation of **3** were overcome by employing its derived thallous salt with refluxing methyl iodide to give the N-Me dione **6**.

Irradiation of the unsubstituted dione **3** in benzene, followed by recrystallization of the resultant precipitate from acetone, gave the dimer, **5**.

In contrast, irradiation of the N-Me dione, **6**, led to a complex mixture of products. Chromatography on silica gel afforded the pure dimer **7** as the major product.

The structural assignments of the photodimers **5** and **7** follow from their NMR spectra. Thus, decoupling experiments with **5** (Table 1) established the following relationship among the cyclobutane protons: (a) the H_1 proton resonance at δ 4.93 was coupled to two doublets of doublets at δ 4.19 (H_3) and 3.95 (H_4); (b) the H_4 proton doublet of doublets at δ 3.95 was coupled to multiplets at δ 4.93 (H_1) and 4.43 (H_2) and (c) the H_2 multiplet at δ 4.43 was coupled to two doublets of doublets at δ 3.95 (H_4) and 4.19 (H_3). Similarly, in the case of **7**, the irradiation of the H_4 proton doublet of doublets at δ 3.04 and the H_3 proton doublet of doublets at δ 4.17 established the relationships between the δ 3.04 (H_4), 4.17 (H_3) and 4.88 (H_1) and between the δ 4.17 (H_3) and 4.34 (H_2) resonances, respectively. The chemical shift assignments of protons H_1 and H_2 adjacent to the phenyl rings in **5** and **7** are based on the observed allylic-type interactions. In addition, the highly shielded δ 6.82 multiplet was found to be coupled to δ 7.70 multiplet through a small coupling constant, and thus may be assigned to a phenyl proton para to the carbonyl group in one of the aromatic rings in **7**.



Scheme 1.

Tentative assignment of the stereochemistry follows from an analysis of the coupling constants. Gamba and Mondelli[7] have suggested that in cyclobutane rings the sign of the cross-ring four-bond couplings (^4J) is a more reliable indicator of the *cis-trans* orientation of the interacting protons than is the amplitude of the vicinal couplings (^3J), which are dependent upon substituents, dihedral angles (Karplus Equation) and ring distortions. Specifically, ^4J is positive when coupled protons are *cis* and negative when *trans*. Analysis of the coupling constants (Table 1) of **5** and **7** suggests a syn-anti-syn geometry about the cyclobutane ring. Although the very small values for ^4J make the significance of the determination of sign tenuous, nevertheless the small absolute values are consistent with the structure. Mechanistically, only two such syn-anti-syn photodimers are possible, consisting of two monomeric units juxtaposed in either a parallel (head-to-head) or antiparallel (head-to-tail) fashion.[8] Steric considerations preclude the formation of two other possible products possessing the head-to-head or head-to-tail syn-*cis*-syn geometry. However the most difficult task was the assignment of coupling constants to protons H_1H_4 which was fortunately resolved by considering the NMR spectra of olefins **3** and **6**. Both H_1 and H_4 exhibit proton resonances with trans coupling constants of 12.5 Hz. Thus, protons H_1H_4 are trans in **5** and **7**. The resonances due to protons H_1 and H_2 are slightly broadened as a result of long-range interactions with the aromatic ring protons. Based upon these considerations, the structures **5** and **7** are assigned as head-to-tail and head-to-head, respectively.[10]

With regard to **7**, shift reagent studies [Eu(fod)$_3$-d_{30}, $CDCl_3$] resulted in downfield shifts of the order,[9] NCH_3 (11) > H(ar)-*o*-CO (9) > $H_4 \geq H_1$ (8) > H_3 (7) > H_2 (4) > H(ar)-*o*-CO (3) > NCH_3 (2). This order is interpreted as a selective coordination of the reagent to one of the $CONCH_3$ moieties, with protons H_4 and H_1 being *cis* to the binding site, while H_2 is farther removed. These results support the assignments of the head-to-head geometry **7** to the major N-Me photodimer. While isomer **5** proved too insoluble for shift reagent studies, the reverse addition method gave the following order of downfield shifts, H_2 (5) > $H_1 = H_3$ (4) > H_4 (2). This suggests interaction of the reagent with a CONH group which is closer to H_2 and H_3 and farther from H_4 as in **5**.

The present assignments, **5** and **7**, possess the following unique features: (a) the negative ^4J values, (b) ^3J *cis* overlap ^3J *trans* values and (c) the values of the spectral parameters[11] K, L, M and N; specifically, K = 5.36 and N = 7.71 Hz (hh isomer, **7**) and K = −0.21 and N = 19.11 Hz (ht isomer, **5**).[11]

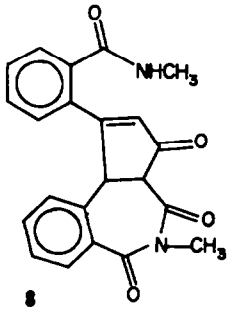
Minor products. The minor, insoluble photoproduct from **3** exhibited unusual behavior by being insoluble in all common organic NMR solvents. The IR, MS and elemental analysis were identical with those of the major isomer **5**. The NMR spectrum in TFA, however, had a C-2 symmetry. It is conceivable that in this case, all protons of the cyclobutane ring are *cis* with a head-to-tail structure. On the other hand, the minor dimer of **6** indicated the presence of $CONHCH_3$ moiety in the NMR spectrum and NH absorption at 3360 cm^{-1} in IR. The mass spectrum indicated the loss of *m/e* 31 (CH_3NH_2) and lacked the *m/e* 187 assigned to cyclobutane fragmentation in the major isomer **7**. Shift reagent studies did not provide further insight into the structure. A plausible structure **8**, is proposed for this minor product.

Attempted methylation of **5** *to* **7**. Several experiments using various conditions such as, (a) MeI/CaO in DMSO, (b) MeI/benzyltriethylammonium chloride (2 equiv)/aq NaOH in $CHCl_3$, (c) MeI/AgO in DMF, (d) MeI/K_2CO_3 in DMF, (e) MeI/K-*t*-BuOH in THF and (f) MeI/NaH in DMF[12] were attempted to methylate **5**. With the exception of the last experiment, only a mono N-Me product was obtained. This compound possessed

Table 1. NMR analysis of the major photodimers (δ, ppm from TMS)

Compound	Coupling Constants						Chemical Shifts			
	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}	H_1	H_2	H_3	H_4
5 (C_5D_5N)	−0.11*	10.58	12.03	8.53	9.07	−0.10*	4.93	4.43	4.19	3.95
7 ($CDCl_3$)	0.33	−0.03*	12.28	7.74	−0.29*	5.03	4.88	4.34	4.17	3.04

The J values in Hz were obtained from analysis of cyclobutane protons as $H_1H_2H_3H_4$ system utilizing LAOCOON II [S. Castellano and A. A. Brothner - By, *J. Chem. Phys.*, 41, 3869 (1967)] and KMREN-NMRIT [J. D. Swalen and C. A. Reilly, *ibid*, 37, 21 (1962)] programs. The RMS errors are less than 0.01. *Cross-ring (^4J) coupling constants.



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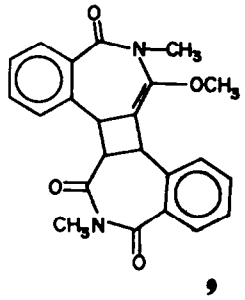

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Scheme 2.

significantly increased solubility in $CHCl_3$ and exhibited no change in stereochemistry of the cyclobutane protons (NMR). The product obtained in the last experiment gave an elemental analysis consistent with that of a trimethyl derivative. The NMR, TLC (silica gel; $CHCl_3$: EtOAc, 98:2) and m.p. were different from those of either 7 or its minor isomer 8. The NMR ($CDCl_3$) exhibited three Me resonances at δ 2.55, 3.38 and 3.65 with the simultaneous loss of one cyclobutane proton resonance. These results are consistent with two N-Me and one O-Me groups and with the tentative assignment of structure 9 to the latter product.

EXPERIMENTAL

M.ps were determined on a Thomas–Hoover apparatus and are uncorrected. IR spectra were obtained with a Perkin–Elmer 621 spectrophotometer. The NMR spectra were obtained with Varian XL-100-15 NMR spectrometer internally locked to ^2H frequency of the solvent. For 5, a 220 MHz NMR spectrum in pyridine-d_5 was obtained from Dr. M. Shaeffer of Montreal, Canada.

2-(Chloroformyl)-cis-cinnamonitrile, 1. To a rapidly stirring suspension of P_2O_5 (197.5 g; 0.95 mol) in 3.5 l dry hexane was added portionwise 167.0 g (0.96 mol) 2-nitroso-1-naphthol. The mixture was stirred at room temp. for 1 hr and then heated under reflux for 1 hr. The hot soln was decanted after slight cooling. The residue was re-extracted with 3.0 l. hexane for 1 hr after which the soln was decanted. The combined hexane extract was evaporated to dryness to give 200.0 g crude product. The crude product was extracted with 2.0 l. hexane, the extract was cooled and the crystals which formed were filtered off. The filtrate was used to re-extract the desired compound from the above residue four-times, cooling and filtering off the crystals obtained each time, yield: 79.0 g (42.5%), m.p. = 72–74°.

2H-2-Benzazepine-1,3-dione, 3. A soln containing 1 (59.0 g; 0.31 mol) in 800 ml dioxane at 70° was purged with HCl gas for 5 hr. After evaporating off the solvent, the residue was azeotroped with benzene three times and finally dissolved in 200 ml 1,2-dimethoxyethane and 22 ml water. This soln was allowed to stand overnight at room temp., evaporated to dryness and the residue dissolved in 1.0 l. EtOAc. This organic soln was washed with 630 ml portions sat $NaHCO_3$ aq. The $NaHCO_3$ phase was washed with 1.0 l. EtOAc and the combined organic extract was washed three times with 500 ml portions water. The solvent was evaporated and the solid was dissolved in 1.0 l. acetone, treated with charcoal and the acetone evaporated off. Recrystallization of the product from a benzene (500 ml) and petroleum ether (650 ml) mixture gave a yield of 20.7 g (37%); single spot, R_f 0.30 (alumina, $CHCl_3$: EtOAc = 6:4); m.p. = 135–136°; *m/e* = 173; NMR ($CDCl_3$) δ 6.37 (1H, dd, J = 12.5 and 2.5 Hz, =CHC=O), 7.11 (1H, d, J = 12.5 Hz, Ar–CH=), 7.45 (1H, m), 7.62 (2H, m), 8.52 (1H, m, J = 8.0, 1.5 and 0.5 Hz, ArH-*o*-CO) and 8.92 (1H, b, NH).

Irradiation at δ 8.90 eliminated the J_{CH-NH} coupling constant of 2.5 Hz from δ 6.37 resonance. (Found: C, 69.25; H, 4.29; N, 8.30. Calc. for $C_{10}H_7O_2N$: C, 69.36; H, 4.07; N, 8.09%).

2-Methyl-2H-2-benzazepin-1,3-dione, 6. A soln containing 3 (6.0 g; 0.035 mol) in 200 ml dry THF was stirred with 10.80 g (0.043 mol) thallium ethoxide (TlOEt) for 30 min. The ppt was filtered off, washed with ether and dried in a vacuum oven at room temp. for 30 min. The thallium salt thus obtained was suspended in 60 ml MeI and the mixture refluxed for 5 hr under argon. The mixture was cooled and the excess MeI was evaporated with argon. The yellow solid thus obtained was stirred with 100 ml benzene for 40 min, filtered off and washed with 100 ml benzene. The combined filtrate was passed through a Florisil column and the column eluted with 100 ml benzene. The elute was evaporated to dryness, yield: 5.4 g (86%); single spot (alumina, $CHCl_3$: EtOAc–6:4); m.p. = 67–68°; *m/e* = 187; IR (KBR) 5.87 and 5.93 μ (C=O stretch); NMR ($CDCl_3$) δ 3.49 (3H, s, NCH_3), 6.44 (1H, d, J = 12.5 Hz, =CH–C=O), 7.02 (1H, d, J = 12.5 Hz, Ar–CH=), 7.45 (1H, m), 7.57 (2H, m) and 8.28 (1H, m, J = 8.0, 1.5 and 0.5 Hz, ArH-*o*-CO). (Found: C, 70.84; H, 5.03; N, 7.47. Calc. for $C_{11}H_9O_2N$: C, 70.58; H, 4.85; N, 7.48%).

7a,14b,7b,14a - trans - 7a,7b,14a,14b - Tetrahydrocyclobuta[1,2-d:3,4 - d']bis[2] benzazepine - 5,7,12,14(6H,13H) - tetrone, 5. A soln of 3 (1.58 g; 0.009 mol) in 250 ml spectral grade benzene was purged with N_2 and then irradiated with a Hanovia 450 Watt medium pressure Hg lamp, through a Pyrex, water-cooled probe for 3 hr. The product was filtered off and extracted in a Soxhlet extractor with 400 ml acetone. The acetone extract was filtered and evaporated to give 1.02 g (yield = 70%) of solid. Recrystallization from acetone gave 0.75 g pure product with m.p. 336–345° dependent on heating rate; shrinks at *ca.* 250°, "brown" at *ca.* 315°, decomposes at 336–345°; *m/e* = 346; IR (KBr) 2.98 μ (NH stretch), 5.78, 5.86 and 5.98 μ (C=O stretch); UV (95% EtOH) ϵ 465 at 238 mμ and 98.5 at 284 mμ; NMR (C_5D_5N) δ 3.95 (1H, dd, J = 12.0 and 9.0 Hz), 4.19 (1H, dd, J = 10.5 and 8.0 Hz), 4.43 (1H, dd, J = 9.0 and 8.0 Hz), 4.93 (1H, dd, J = 12.0 and 10.0 Hz), 7.40–7.50 (6H, m), 8.23 (1H, dd, J = 6.0 and 2.0 Hz, ArH-*o*-CO), 8.41 (1H, dd, J = 7.0 and 2.0 Hz, ArH-*o*-CO) and 6–7 (broad, NH). (Found: C, 69.16; H, 4.11; N, 7.90. Calc. for $C_{20}H_{14}O_4N_2$: C, 69.36; H, 4.07; N, 8.09%).

The insoluble material, "Insoluble Isomer", (476 mg) was removed from the Soxhlet cup, boiled with 175 ml acetone and filtered while hot, yield = 203 mg; m.p. = 330–334°; *m/e* = 346; IR (KBr) 2.98 μ (NH stretch), 5.78, 5.86 and 5.98 μ (C=O stretch); UV (95% EtOH) ϵ 405 at 240 mμ (sh) and 96.3 at 283 mμ; NMR (TFA) δ 4.40 (4H, s), 6.95 (1H, dd, J = 6.0 and 3.0 Hz), 7.52 (5H, m) and 8.22 (2H, J = 6.0 and 3.0 Hz, ArH-*o*-CO). (Found: C, 69.10; H, 4.35; N, 7.85. Calc. for $C_{20}H_{14}O_4N_2$: C, 69.36; H, 4.07; N, 8.09%).

7a,14b;7b,14a - trans - 7a,7b,14a,14b - Tetrahydro - 6,12 - dimethylcyclobuta[1,2 - d:3,4 - d']bis[2] - benzazepin - 5,7,12,14(6H,13H) - tetrone, 7. A soln of 6 (2.63 g; 0.014 mol) in 750 ml spectral grade benzene was purged with N_2 for 10 min and irradiated as described for 5 for 6 hr. The soln was concentrated to *ca.* 50 ml and the suspension was treated with 55 ml hexane, dropwise. The ppt was filtered off, dried and chromatographed on 36 g of Woelm silica gel (18 × 292 mm column) starting with 1000 ml CH_2Cl_2, followed by 200 ml CH_2Cl_2:$CHCl_3$ (1:1) and then 200 ml $CHCl_3$. These fractions were discarded and the next 600 ml $CHCl_3$ were evaporated to give 2.06 g crude product (80% yield). Recrystallization (at −20°) from *ca* 1.2 l. of abs EtOH gave 0.45 g pure product, m.p. 273–274°, *m/e* = 374; IR (KBr) 5.61, 5.86 and 6.06 μ (C=O stretch); UV (95% EtOH) ϵ 261 at 239 mμ and 47 at 280 mμ; NMR ($CDCl_3$) δ 3.04 (1H, dd, J = 12.0 and 5.0 Hz), 4.17 (1H, dd, J = 8.0 and 5.0 Hz), 4.34 (1H, d, J = 8.0 Hz), 4.88 (1H, d, J = 12.0 Hz), 2.84 (3H, s, NCH_3), 3.54 (3H, s, NCH_3), 6.82 (1H, m, J = 7.5, 6.0 and 3.5 Hz), 7.30 (5H, m), 7.70 (1H, dd, J = 8.0 and 3.5 Hz, ArH-*o*-CO) and 7.81 (1H, dd, J = 9.0 and 3.5 Hz). (Found: C, 70.85; H, 5.15; N, 7.60. Calc. for $C_{22}H_{18}O_4N_2$: C, 70.58; H, 4.85; N, 7.48%).

The filtrate from the above was concentrated to *ca.* 800 ml, cooled in the freezer and filtered. This process was repeated twice while reducing the filtrate to *ca.* 500 ml. Finally the filtrate was concentrated to *ca.* 75 ml, cooled in the freezer and the minor product was filtered off and dried, wt = 0.33 g; m.p. 222–224°, *m/e* = 374; IR ($CDCl_3$) 3360 cm^{-1} (NH stretch), 1705, 1640 cm^{-1} (C=O stretch) and 1680, 1595 cm^{-1} (amide C=O stretch); UV (95% EtOH) ϵ 420 at 253 mμ and 371 at 260 mμ; NMR ($CDCl_3$) δ 2.57 (3H, d, J = 5.0 Hz, becomes singlet on CD_3OD exchange, $NHCH_3$), 3.47 (3H, s, NCH_3), 4.07 (1H, d, J = 6.5 Hz, –CH–CH–), 4.31 (1H, d, J = 6.5 Hz, –CH–CH–), 4.09 (1H, s, CH), 7.55 (1H, s, exchanges slowly with CD_3OD, NH), 7.30–7.76 (7H, m) and 7.90 (1H, dd, J = 7.0 and 1.0 Hz, ArH-*o*-CO). (Found: C, 70.46; H, 4.15: N, 7.39. Calc. for $C_{22}H_{18}O_4N_2$: C, 70.58; H, 4.85; N, 7.48%).

Attempted methylation of 5

(a) A soln containing 5 (0.173 g; 0.5 mmol) dissolved in 5 ml dry DMSO was treated with 6.7 g (47 mmol) MeI followed by addition of 2.0 g CaO and 1.0 g Drierite. The mixture was stirred at room temp. for 6.5 hr, filtered and the solid washed with 2 ml dry DMSO. The excess MeI was removed from the filtrate at room temp. The remaining viscous soln was then poured onto 150 ml ice-water, stirred and filtered, yielding 180 mg solid. The major band, separated by TLC, gave analytical data consistent with a mono Me derivative, yield: 51 mg; m.p. 234–5°; IR (KBr)

3200 cm^{-1} (NH stretch), 1700, 1640 cm^{-1} (C=O stretch); NMR ($CDCl_3$) δ 3.40 (3H, s, NCH_3), 3.59 (1H, dd, J = 12.0 and 8.0 Hz), 3.97 (1H, dd, J = 11.0 and 9.0 Hz), 4.27 (1H, dd, J = 9.0 and 8.0 Hz), 4.56 (1H, dd, J = 12.0 and 11.0 Hz), 7.12 (1H, dd, J = 7.0 and 1.0 Hz), 7.48 (5H, m), 7.89 (1H, m) and 8.22 (2H, m, ArH-*o*-CO). (Found: C, 66.46; H, 4.49; N, 7.01. Calc. for $C_{21}H_{16}O_4N_2$: C, 69.60; H, 4.44; N, 7.73%).

(b) A soln containing 5 (150 mg; 0.43 mmol) in 5.0 ml distilled DMF was cooled to 0–5° and treated with 0.051 g (1.1 mmol) 56% NaH oil dispersion. The mixture was warmed to room temp. and stirred for 2 hr. After cooling to 0°, 3.42 g (25 mmol) of MeI was added and the reaction was stirred at room temp. for 65 hr. It was then poured into 50 ml H_2O, stirred and extracted two times with 50 ml portions CH_2Cl_2. The organic extract was dried over Drierite, the solvent evaporated and the solid was separated by TLC (silica gel; $CHCl_3$: EtOAc = 98:2), yield: 58 mg; m.p. 245–7°; IR (KBr) 1652, 1702 cm^{-1} (C=O stretch), 987, 1031, 1072 cm^{-1}; NMR ($CDCl_3$) δ 2.55 (3H, s, NCH_3), 3.38 (3H, s, OCH_3), 3.52 (1H, m, J = 0.5 Hz) 3.65 (3H, s, NCH_3), 3.77 (1H, dd, J = 6.0 and 0.5 Hz), 4.14 (1H, d, J = 6.0 Hz) and between 7.32–7.60 (8H, m, aromatic protons); NMR (C_6D_6) δ 2.55 (3H, s, NCH_3), 2.65 (1H, m, J = 0.5 and 0.5 Hz), 3.09 (3H, s, CH_3), 3.27 (3H, s, CH_3), 4.33 (1H, d, J = 6.5 Hz), 4.62 (1H, d, J = 6.5 Hz), 6.94 (7H, m, aromatic protons) and 7.66 (1H, dd, J = 7.0 and 1.0 Hz, ArH-*o*-CO). (Found: C, 70.84; H, 5.06; N, 7.28. Calc. for $C_{23}H_{20}O_4N_2$: C = 71.16, H = 5.19; N = 7.22%).

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[10]The deviations in the NMR behavior of the H_1H_2 and the H_3H_4 protons from that expected of a compound possessing either a plane of symmetry (in dimer 7) or a center of symmetry (in dimer 5) are attributed to the mobility of the seven membered rings. Both rings in each dimer may adopt conformations different from each other to minimize steric interactions. This results in strain on the cyclobutane ring causing non-equivalence of the protons in the NMR. The difference in the photochemical behavior of 3 and 6 is attributed to the ability of the former compound to enolize and perhaps dimerize as a hydroxy derivative. In contrast the presence of the N-methyl group prohibits this process in 6.

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